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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		DATE: January 14, 2002
		U.S. APPL. NO. (IF KNOWN, REF. TO C.F.R. 1.53) Not Yet Assigned 10030088
INTERNATIONAL APPLICATION NO. PCT/JP00/04717	INTERNATIONAL FILING DATE 13 July 2000	PRIORITY DATE CLAIMED 14 July 1999
TITLE OF INVENTION: HEAT-RESISTANT EXPANDED GRAPHITE SHEET AND METHOD FOR PRODUCTION OF THE SAME		
APPLICANT(S) FOR DO/EO/US: SAKAIRI, Yoshikazu; SHIMURA, Toshihiko; KUROSE, Kohei; KUSUYAMA, Toshiaki; INOMOTO, Hideki; KAKIMI, Hideaki		
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. (THE BASIC FILING FEE IS ATTACHED)</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures [35 U.S.C. 371(f)] at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</p> <p>4. <input type="checkbox"/> A proper demand for International Preliminary Amendment was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed [35 U.S.C. 371(c)(2)]</p> <p>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> A translation of the International Application into English [35 U.S.C. 371(c)(2)].</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 [35 U.S.C. 371(c)(3)]</p> <p>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</p> <p>b. <input type="checkbox"/> have been transmitted by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 [35 U.S.C. 371(c)(3)].</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) [35 U.S.C. 371(c)(4)].</p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 [35 U.S.C. 371(c)(5)].</p> <p>Items 11 - 16 below concern other document(s) or information included:</p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input checked="" type="checkbox"/> Other items or information: <input checked="" type="checkbox"/> PCT/IB/301; PCT/IB/304; PCT/IB/308; PCT/IB/332; PCT/RO/101; PCT Application in Japanese Drawings (1 sheets)</p>		

U.S. APPIN NO (IF KNOWN) **10703**
SEE 37 C.F.R. 1.50) Not Yet Assigned

ATTORNEY DOCKET NO. 107312-00001

DATE: January 14, 2002

17. ☒ The following fees are submitted:

Basic National Fee [37 C.F.R. 1.492(a)(1)-(5)]:
Search Report has been prepared by the EPO or JPO.....\$890.00
International preliminary examination fee paid to USPTO
[37 C.F.R. 1.482).....\$710.00
No international preliminary examination fee paid to USPTO
[37 C.F.R. 1.482) but international search fee paid to USPTO
[37 C.F.R. 1.445(a)(2)].....\$740.00
Neither international preliminary examination fee
[37 C.F.R. 1.482) or international search fee
[37 C.F.R. 1.445(a)(2)] paid to USPTO.....\$1,040.00
International preliminary examination fee paid to USPTO
[37 C.F.R. 1.482) and all claims satisfied provisions of
PCT Article 33(2)-(4).....\$ 100.00

CALCULATIONS PTO USE ONLY

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date [37 C.F.R. 1.492(e)].

\$ 0.00

Claims	Number Filed	Number Extra	Rate
Total Claims	8 - 20 =	0	X \$ 18.00
Independent Claims	3 - 3 =	0	X \$ 84.00
Multiple dependent claim(s) (if applicable)			+ \$280.00

TOTAL OF ABOVE CALCULATIONS =

\$ 890.00

Reduction by one-half for filing by small entity, if applicable.
Verified Small Entity statement must also be filed.
(Note 37 C.F.R. 1.9, 1.27, 1.28).

\$ 0.00

SUBTOTAL =

\$ 890.00

Processing fee of \$130.00 for furnishing the English translation
later the ☐ 20 ☐ 30 months from the earliest claimed priority date
[37 C.F.R. 1.492(f)].

\$ 0.00

TOTAL NATIONAL FEE =

\$ 890.00

Fee for recording the enclosed assignment [37 C.F.R. 1.21(h)]. The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. 3.28, 3.31). \$40.00 per property +

\$ 0.00

TOTAL FEES ENCLOSED =

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- a. ☒ A check in the amount of \$890.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. 01-2300 in the amount of \$_____ to cover the above fee.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-2300.

NOTE: Where an appropriate time limit under 37 C.F.R. 1.494 or 1.495 has not been met, a petition to revive [37 C.F.R. 1.137(a) or (b)] must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO.

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10/030088 #3/a
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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:
T. SHIMURA et al.

Appln. No.: PCT/JP00/04717

Filed: Concurrently herewith

Attorney Dkt. No.: 107312-00001

For: HEAT-RESISTANT EXPANDED GRAPHITE SHEET AND METHOD FOR
PRODUCTION OF THE SAME

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

January 14, 2002

Sir:

Prior to calculation of the filing fees and initial examination of the application,
please amend the above-identified application as follows:

IN THE CLAIMS:

Please amend claims 3, 4, and 7-9 as follows:

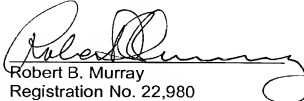
3. (Amended) The heat-resistant, expanded graphite sheet according to claim 1,
wherein the phosphate is selected from monobasic lithium phosphate, dibasic lithium
phosphate, monobasic calcium phosphate, dibasic calcium phosphate, monobasic
aluminum phosphate and dibasic aluminum phosphate.
4. (Amended) The heat-resistant, expanded graphite sheet according to claim 1,
wherein the sheet is less than 10% in the oxidative ablation factor on exposure to the air
at a temperature of 700°C for 3 hours.

7. (Amended) The method according to claim 5, wherein the phosphoric acid is selected from orthophosphoric acid, metaphosphoric acid, polyphosphoric acid and polymetaphosphoric acid.
8. (Amended) The method according to claim 5, wherein the phosphate is selected from monobasic lithium phosphate, dibasic lithium phosphate, monobasic calcium phosphate, dibasic calcium phosphate, monobasic aluminum phosphate and dibasic aluminum phosphate.
9. (Amended) A heat-resistant, expanded graphite sheet prepared by the method for producing a heat-resistant, expanded graphite sheet according to claim 5, wherein the sheet contains 0.05 to 5.0% by weight of phosphorus pentoxide, and 1 to 16% by weight of phosphate.

REMARKS

Claims 1-9 are pending in this application. By this Amendment, claims 3,4 and 7-9 are amended to correct the multiple dependency thereof and to place this application into better condition for examination. No new matter is added.

Respectfully submitted,


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CLAIMS:

1. A heat-resistant, expanded graphite sheet containing phosphorus pentoxide and phosphate.
2. The heat-resistant expanded graphite sheet
5 according to claim 1, wherein the content of phosphorus pentoxide is 0.05 to 5.0% by weight and the content of phosphate is 1 to 16% by weight.
3. The heat-resistant, expanded graphite sheet according to claim 1 *or 2* wherein the phosphate is
10 selected from monobasic lithium phosphate, dibasic lithium phosphate, monobasic calcium phosphate, dibasic calcium phosphate, monobasic aluminum phosphate and dibasic aluminum phosphate.
4. The heat-resistant, expanded graphite sheet
15 according to *Claim 1* any one of claims 1 to 3 wherein the sheet is less than 10% in the oxidative ablation factor on exposure to the air at a temperature of 700°C for 3 hours.
5. A method for producing a heat-resistant, expanded graphite sheet, the method comprising adding phosphate to
20 an acid-treated graphite material treated with a strong acid and phosphoric acid.
6. A method for producing a heat-resistant, expanded graphite sheet, the method comprising adding phosphoric acid and phosphate to an acid-treated graphite material
25 treated with a strong acid.

1/PATS

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HEAT-RESISTANT EXPANDED GRAPHITE SHEET AND
METHOD FOR PRODUCTION OF THE SAME

Field of the Invention

The present invention relates to an expanded
5 graphite sheet and a method for producing the same, and
more particularly to an expanded graphite sheet which is
excellent in heat resistance and resistance to oxidative
ablation and a method for producing the same.

Background Art

10 An expanded graphite sheet can be prepared as
follows. For example, graphite such as natural graphite,
kish graphite, pyrolytic graphite or the like is treated
with concentrated sulfuric acid, concentrated nitric acid,
concentrated sulfuric acid and potassium chlorate,
15 concentrated sulfuric acid and potassium nitrate or
hydrogen peroxide or like strong oxidizing agents, bromine
or aluminum chloride or like halides to form an
interlaminar compound, and rapidly heating fine particles
of graphite incorporating the interlaminar compound (acid-
20 treated graphite material), for example, at a temperature
of 950°C or higher for 1 to 10 seconds to emit a cracked
gas, whereby the interlaminar crevice of graphite is
expanded by the pressure of the gas to produce expanded
graphite particles. Then, the expanded graphite particles
25 are made into a sheet by compression molding or roll

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molding in the presence or the absence of a binder. The expanded graphite sheet thus formed has excellent properties and is therefore effectively used in wide fields of, e.g., gaskets, sealings, heat-insulating materials, cushion materials and the like.

Among expanded graphite particles conventionally used for this kind of expanded graphite sheet, those of low expansivity, e.g. those expansible to about 20 to about 70 folds entail difficulties in molding the particles into a sheet in the absence of a binder, consequently necessitating the use of an adhesive, which raises problems of lowering the purity and degrading the properties due to the adhesive.

On the other hand, when using expanded graphite particles of high expansivity, e.g. those expansible to about 200 to about 300 folds, the obtained sheets can be formed from only graphite so that the sheet is highly pure and outstanding in properties. For this reason, generally expanded graphite particles of high expansivity are used today in the manufacture of expanded graphite sheets.

However, conventional expanded graphite sheets pose a problem of low heat resistance in the air, especially in the air at a temperature as high as 700°C or more, leading to oxidative ablation of graphite. Namely conventional sheets have a serious drawback of involving a

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high oxidative ablation factor.

In order to overcome the problem, expanded graphite sheets have been developed by a process wherein low-expansivity graphite particles are treated with phosphoric acid or phosphate for suppressing the oxidation (JP-B-54-30678). The publication discloses that the intended sheet can be formed from low-expansivity graphite particles by using phosphoric acid or phosphate without use of an adhesive. However, although the particles can be molded into sheets, the obtained sheets are unsatisfactory in the properties required by expanded graphite sheets such as mechanical properties and uniformity of sheets because of lack of an adhesive. In addition, the publication also describes that the resistance to oxidation is improved. But the improvement was found insufficient. Especially when the sheet is exposed to the air at a high temperature for a long time, it suffers from an intensive oxidative ablation. In short, the disclosed sheets are far from satisfactory.

The invention has been completed to obviate the foregoing problems. Thus, an object of the invention is to provide an expanded graphite sheet which shows a low oxidative ablation factor in the air even when exposed to the air under high temperature conditions of 700°C or more for a long time, the sheet being excellent in heat resistance and favorable in other properties as required by

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this kind of expanded graphite sheet, and also a method for preparing the same.

Disclosure of the Invention

The inventors of the invention conducted
5 extensive research to achieve the above-mentioned object and found that expanded graphite sheets containing phosphorus pentoxide and phosphate in specified proportions are superior in heat resistance, low in the oxidative ablation factor in the air even on exposure to the air
10 under high temperature conditions of 700°C or higher for a long time and satisfactory in other properties required by this kind of expanded graphite sheet. The present invention was accomplished based on these findings. The summary of the invention is as follows.

15 A heat-resistant, expanded graphite sheet according to a first embodiment of the invention contains phosphorus pentoxide and phosphate.

The heat-resistant, expanded graphite sheet according to the first embodiment of the invention contains
20 phosphorus pentoxide and phosphate so that the sheet is remarkable in heat resistance and low in the oxidative ablation factor in the air even on exposure to the air under high temperature conditions of 700°C or higher for a long time and can be applied for various purposes under
25 high temperature conditions. The sheets have the properties

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required by this kind of expanded graphite sheet and are satisfactory in other properties.

A heat-resistant, expanded graphite sheet according to a second embodiment of the invention is similar to the expanded graphite sheet of the first embodiment but different from the latter sheet in that the former sheet contains 0.05 to 5.0% by weight of phosphorus pentoxide and 1 to 16% by weight of phosphate.

In the heat-resistant, expanded graphite sheet according to the second embodiment of the invention, the graphite sheet containing less than 0.05% by weight of phosphorus pentoxide can not significantly reduce the oxidative ablation factor, and the sheet containing more than 5.0% by weight thereof fails to lower the oxidative ablation factor. Further when the content of phosphate is less than 1% by weight, the sheet can not sufficiently reduce the oxidative ablation factor, whereas the content of more than 16% by weight tends to harden the sheet, thus resulting in degraded flexibility of the graphite sheet.

A heat-resistant, expanded graphite sheet according to a third embodiment of the invention is similar to but different from the expanded graphite sheet of the first or second embodiment of the invention in that the phosphate incorporated in the former sheet is selected from monobasic lithium phosphate, dibasic lithium phosphate,

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monobasic calcium phosphate, dibasic calcium phosphate, monobasic aluminum phosphate and dibasic aluminum phosphate.

A heat-resistant, expanded graphite sheet

according to a fourth embodiment of the invention is

5 similar to but different from the graphite sheet of any of the first to third embodiments in that the former sheet is less than 10% in the oxidative ablation factor on exposure to the air under high temperature conditions of 700°C for 3 hours.

10 The heat-resistant, expanded graphite sheet according to the fourth embodiment of the invention contains phosphorus pentoxide and phosphate in specified amounts so that the sheet is remarkable in heat resistance and very low in the oxidative ablation factor even on
15 exposure to the air under high temperature conditions for a long time.

A method for producing a heat-resistant, expanded graphite sheet according to a 5th embodiment of the invention comprises the steps of adding phosphate to a
20 acid-treated graphite material treated with a strong acid and phosphoric acid, drying the mixture, subjecting the dried mixture to expansion treatment to give expanded graphite particles, and making the particles into a sheet by compression molding or roll molding.

25 A method for producing a heat-resistant, expanded

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graphite sheet according to a 6th embodiment of the invention comprises the steps of adding phosphoric acid and phosphate to a acid-treated graphite material treated with a strong acid, drying the mixture, subjecting the dried
5 mixture to expansion treatment to give expanded graphite particles, and making the particles into a sheet by compression molding or roll molding.

Useful strong acids include, for example, sulfuric acid. The expansion operation may be conducted
10 preferably by expanding the graphite to about 200 to about 300 folds at an expansion temperature of 900°C or higher, preferably about 950 to about 1200°C.

A method for producing a heat-resistant, expanded graphite sheet according to a 7th embodiment of the
15 invention is similar to but different from the method of the 5th and 6th embodiments of the invention in that the phosphoric acid to be used in the former method is selected from orthophosphoric acid, metaphosphoric acid, polyphosphoric acid and polymetaphosphoric acid.

20 In the method for producing a heat-resistant, expanded graphite sheet according to the 7th embodiment of the invention, the phosphoric acid uniformly dispersed in the acid-treated graphite material forms phosphorus pentoxide (P_2O_5) on dehydration reaction in thermal
25 expansion treatment and it is incorporated in a specified

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proportion throughout the sheet by compression molding or roll molding.

A method for producing a heat-resistant, expanded graphite sheet according to a 8th embodiment of the invention is similar to but different from the method of 5 5th or 6th embodiment in that the phosphate to be used in the former method is selected from monobasic lithium phosphate, dibasic lithium phosphate, monobasic calcium phosphate, dibasic calcium phosphate, monobasic aluminum 10 phosphate and dibasic aluminum phosphate.

In a method for producing a heat-resistant, expanded graphite sheet according to a 9th embodiment of the invention, the phosphate uniformly incorporated in the acid-treated graphite material is dispersed as the 15 phosphate throughout the sheet with substantially no change in the thermal expansion treatment. Consequently the heat-resistant, expanded graphite sheet produced by the method contains specified proportions of phosphorus pentoxide and phosphate.

20 The mode for carrying out the invention will be described in more detail.

The method for producing a heat-resistant, expanded graphite sheet will be described.

The term "acid-treated graphite material" used 25 herein refers to a raw material conventionally used which

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is prepared by treating graphite with sulfuric acid and an oxidizer by conventional methods and drying the treated graphite in the conventional manner. Stated more specifically, graphite is treated with a known oxidizer
5 such as hydrogen peroxide or the like and with a strong acid such as sulfuric acid, and the treated graphite is dried at about 100 to about 120°C in the conventional manner. The invention includes a graphite material treated with phosphoric acid together with sulfuric acid. The acid-
10 treated graphite material will be described in more detail.

(A) Graphite material treated with sulfuric acid

(B) Graphite material treated with sulfuric acid and phosphoric acid

In the present invention, any one of the above-mentioned
15 acid-treated graphite materials is used.

Using any of these acid-treated graphite materials, in the case of A, phosphoric acid and phosphate are added at the same time, or phosphoric acid is added first, and phosphate is added; or optionally in the case of
20 B, phosphate is added. Thereafter, the graphite is expanded in the conventional manner to about 200 to about 300 folds preferably at an expansion temperature of about 950 to about 1200°C, and is made into a sheet.

Extensively usable as this kind of graphite are a
25 variety of graphite materials such as natural graphite,

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kish graphite and pyrolytic graphite which have been conventionally employed.

The phosphoric acid to be uniformly incorporated into the acid-treated graphite powder is selected from
5 orthophosphoric acid (H_3PO_4), metaphosphoric acid (HPO_3), polyphosphoric acid, more specifically pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) and tripolyphosphoric acid ($\text{H}_5\text{P}_3\text{O}_{10}$) and like chain condensed phosphoric acids, polymetaphosphoric acid, more specifically trimetaphosphoric acid, tetrametaphosphoric
10 acid and like cyclic condensed phosphoric acids. These phosphoric acids are used in the form of an aqueous solution.

Examples of phosphate to be uniformly dispersed along with phosphoric acid are monobasic phosphate and
15 dibasic phosphate, preferably alkali metal salts and alkaline earth metal salts, more preferably lithium and calcium. Aluminum salts are also usable as metal salts. Specific examples are monobasic lithium phosphate (LiH_2PO_4), dibasic lithium phosphate (Li_2HPO_4), monobasic calcium
20 phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$], dibasic calcium phosphate (CaHPO_4), monobasic aluminum phosphate [$\text{Al}(\text{H}_2\text{PO}_4)_3$], dibasic aluminum phosphate [$\text{Al}_2(\text{HPO}_4)_3$], etc. These phosphates are used in the form of an aqueous solution or a suspension.

Thereafter the expanded graphite material is
25 treated preferably at a temperature of 950 to 1200°C for

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about 1 to about 10 seconds to give off a cracked gas, whereby the interlaminar crevice of graphite is expanded by the gas pressure to provide graphite particles expanded to about 200 to about 300 folds, and the expanded graphite
5 particles are made into a sheet by compression molding or roll molding.

The thus-obtained expanded graphite sheet contains phosphate and the phosphorus pentoxide (P_2O_5) generated by dehydration reaction of phosphoric acid. The heat resistance
10 and the oxidative ablation factor of the expanded graphite sheet are variable depending on the contents of phosphorus pentoxide and phosphate present in the sheet.

It was confirmed in the invention that an expanded graphite sheet is superior in heat resistance and
15 in resistance to oxidative ablation when the sheet contains 0.05 to 5.0% by weight, preferably 0.2 to 2.0% by weight, of phosphorus pentoxide and 1 to 16% by weight, preferably 2 to 10% by weight, of phosphate.

The content of less than 0.05% by weight of
20 phosphorus pentoxide in the sheet can not significantly reduce the oxidative ablation factor of the sheet, and the content of more than 5.0% by weight thereof is unlikely to markedly lower the oxidative ablation factor of the sheet and, what is worse, is responsible for emission of white
25 smoke on formation of phosphorus pentoxide by dehydration

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reaction of phosphoric acid, resulting in undesirable environment in terms of hygiene.

When the content of phosphate is less than 1% by weight, the oxidative ablation factor is not sufficiently
5 reduced, whereas the content of more than 16% by weight tends to harden a graphite sheet on formation of graphite sheet, thus resulting in degraded flexibility of graphite sheet.

The expanded graphite sheet of the invention
10 which contains 0.05 to 5.0% by weight of phosphorus pentoxide and 1 to 16% by weight of phosphate has the following properties:

thickness (mm): 0.2 to 1.5

bulk density (g/cm^3): 0.8 to 1.1

15 tensile strength (kgf/cm^2 , %): 40 to 60

compressibility (70 kgf/cm^2 , %): 10 to 25

recovery (70 kgf/cm^2 , %): 25 to 45

Fig.1 shows the results of a test for oxidative
ablation factor of expanded graphite sheets of the
20 invention containing 4% by weight of phosphate (monobasic aluminum phosphate) and varied amounts of phosphorus pentoxide.

It is apparent from the graph showing the test
results that the expanded graphite sheet containing
25 phosphorus pentoxide and phosphate is less than 10% in the

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oxidative ablation factor and is very low in the weight loss ratio even under severe conditions of 700°C and 3 hours.

Brief Description of the Drawings

5 Fig.1 is the graph showing the results of a test for oxidative ablation factor of expanded graphite sheets containing 4% by weight (constant amount) of phosphate (monobasic aluminum phosphate) and varied amounts of phosphorus pentoxide. The graph shows an oxidative ablation
10 factor of expanded graphite sheets in terms of weight loss ratio which were left to stand in the air maintained at a temperature of 700°C for 3 hours.

 Fig.2 is a view showing an example of a tester for evaluating the flexibility of the graphite sheet.

15 Field of the Invention

 The heat-resistant, expanded graphite sheets of the invention are remarkable in heat resistance and resistance to oxidative ablation and are used for gaskets, sealings, heat-insulating materials, cushion materials or
20 the like.

Best Mode for Carrying out the Invention

 The present invention will be described below in more detail with reference to the following examples to which, however, the invention is not limited insofar as an
25 embodiment is not deviated from the intended scope of the

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invention.

Examples 1 to 20

While stirring 300 parts by weight of concentrated sulfuric acid (conc.98%), 5 parts by weight of .
5 60% aqueous solution of hydrogen peroxide was added as an oxidizing agent to provide a reaction mixture. The reaction mixture was cooled to 10°C and maintained at this temperature. One hundred parts by weight of 30- to 80-mesh natural flaky graphite powder was added. The mixture
10 underwent a reaction for 30 minutes. After the reaction, the acid-treated graphite was separated by suction filtration, and was stirred in 300 parts by weight of water for 10 minutes for suction filtration. This washing operation was repeated twice to remove sufficiently the
15 sulfuric acid portion from the acid-treated graphite.

After sufficient removal of sulfuric acid, the acid-treated graphite was dried for 3 hours in a drying furnace maintained at 110°C to provide an acid-treated graphite material.

20 While stirring 100 parts by weight of the acid-treated graphite material, a solution was sprayed over the acid-treated graphite material, the solution being prepared by diluting, with 10 parts by weight of methanol, 0.16 to 3.5 parts by weight of an aqueous solution of
25 orthophosphoric acid (conc.84%) serving as phosphoric acid,

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and 2 to 38 parts by weight of an aqueous solution of monobasic aluminum phosphate (conc.50%) serving as phosphate. Then, a humid mixture was obtained by uniform stirring.

5 The humid mixture was dried in a drying furnace maintained at 120°C for 2 hours.

 Then the mixture was treated at 1000°C for 5 seconds to give off a cracked gas. The interlaminar crevice in the graphite was expanded by the gas pressure to provide
10 expanded graphite particles (expansion ratio 240 folds). In this expanding operation, the orthophosphoric acid used as one of the components underwent a dehydration reaction to generate phosphorus pentoxide. The monobasic aluminum
15 phosphate was confirmed to co-exist with phosphorus pentoxide with no or little change. The obtained expanded
graphite particles were made into a sheet having a thickness of 0.36 mm by roll molding at a roll space of 0.33 mm.

 The composition of components in the thus-
20 obtained expanded graphite sheet and the results of a test for oxidative ablation factor of the sheet are shown in Tables 1 to 5. The values in the composition of components in the tables are expressed in % by weight.

 The oxidative ablation factor in the expanded
25 graphite sheet was evaluated after allowing the expanded

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graphite sheet to stand in the air maintained at 700°C for 3 hours and was expressed in terms of weight loss ratio (%).

Table 1

	Example			
	1	2	3	4
Expanded graphite	98.9	95.9	93.9	91.9
Phosphorus pentoxide	0.1	0.1	0.1	0.1
Phosphate				
Monobasic aluminum phosphate	1.0	4.0	6.0	8.0
Weight loss ratio	9%	9%	8%	8%

Table 2

	Example			
	5	6	7	8
Expanded graphite	97.8	95.6	93.8	91.8
Phosphorus pentoxide	0.2	0.2	0.2	0.2
Phosphate				
Monobasic aluminum phosphate	2.0	4.0	6.0	8.0
Weight loss ratio	9%	8%	6%	5%

5

Table 3

	Example			
	9	10	11	12

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Expanded graphite	89.8	87.8	85.8	83.8
Phosphorus pentoxide	0.2	0.2	0.2	0.2
Phosphate				
Monobasic aluminum phosphate	10.0	12.0	14.0	16.0
Weight loss ratio	5%	5%	5%	5%

Table 4

	Example			
	13	14	15	16
Expanded graphite	95.6	91.6	95.3	91.3
Phosphorus pentoxide	0.4	0.4	0.7	0.7
Phosphate				
Monobasic aluminum phosphate	4.0	8.0	4.0	8.0
Weight loss ratio	6%	5%	5%	5%

Table 5

	Example			
	17	18	19	20
Expanded graphite	95.0	91.0	94.5	94.0
Phosphorus pentoxide	1.0	1.0	1.5	2.0
Phosphate				
Monobasic aluminum phosphate	4.0	8.0	4.0	4.0
Weight loss ratio	5%	5%	5%	5%

Examples 21 to 28

5

Each acid-treated graphite material was prepared

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in the same manner as in Example 1.

While stirring 100 parts by weight of the acid-treated graphite material, a solution was sprayed over the acid-treated graphite material, the solution being prepared by
5 diluting, with 20 parts by weight of methanol, 0.7 to 1.4 parts by weight of an aqueous solution of orthophosphoric acid (conc.84%) serving as phosphoric acid, and 4.0 to 17.4 parts by weight of an aqueous solution of monobasic calcium phosphate (conc.50%) serving as phosphate. Then, a humid
10 mixture was obtained by uniform stirring. Expanded graphite particles (expansion ratio 240 folds) were prepared in the same manner as in Example 1. Subsequently expanded graphite sheets were produced in the same manner as in Example 1.

The composition of components in the thus-
15 obtained expanded graphite sheet and the results of a test for an oxidative ablation factor of the sheet are shown in Tables 6 and 7. The values in the composition of components in the tables are expressed in % by weight. The oxidative ablation factor in the expanded graphite sheet
20 was evaluated by the same method as in the previous examples.

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Table 6

	Example			
	21	22	23	24
Expanded graphite	97.6	95.6	93.6	91.6
Phosphorus pentoxide	0.4	0.4	0.4	0.4
Phosphate				
Monobasic calcium phosphate	2.0	4.0	6.0	8.0
Weight loss ratio	9%	9%	6%	6%

Table 7

	Example			
	25	26	27	28
Expanded graphite	97.4	95.4	95.2	93.2
Phosphorus pentoxide	0.6	0.6	0.8	0.8
Phosphate				
Monobasic calcium phosphate	2.0	4.0	4.0	6.0
Weight loss ratio	9%	6%	6%	6%

5 Comparative Examples 1 to 5

Each acid-treated graphite material was prepared in the same manner as in Example 1.

While stirring 100 parts by weight of the acid-treated graphite material, 0.3 to 1.7 parts by weight of an aqueous solution of orthophosphoric acid (conc.84%) serving as phosphate was sprayed over the graphite material. Then, a

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humid mixture was obtained by uniform stirring. Expanded graphite particles (expansion ratio 250 folds) were prepared in the same manner as in Example 1. Subsequently expanded graphite sheets were produced in the same manner as in Example 1.

The composition of components in the thus-obtained expanded graphite sheet and the test results as to the oxidative ablation factor of the sheet are shown in Table 8. The values in the composition of components in the tables are expressed in % by weight. The oxidative ablation factor of the expanded graphite sheet was evaluated by the same method as in the previous examples.

Table 8

	Comparative Example				
	1	2	3	4	5
Expanded graphite	99.8	99.6	99.4	99.2	99.0
Phosphorus pentoxide	0.2	0.4	0.6	0.8	1.0
Weight loss ratio	40%	18%	16%	15%	15%

15 Comparative Examples 6 to 9

Each acid-treated graphite material was prepared in the same manner as in Example 1. While stirring 100 parts by weight of the acid-treated graphite material, a solution was sprayed over the acid-treated graphite material, the solution being prepared by

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diluting, with 30 parts by weight of methanol, 8.4 to 38 parts by weight of an aqueous solution of monobasic aluminum phosphate (conc.50%) serving as phosphate. Then, a humid mixture was obtained by uniform stirring. Expanded
 5 graphite particles (expansion ratio 230 folds) were prepared in the same manner as in Example 1. Subsequently expanded graphite sheets were produced in the same manner as in Example 1.

The composition of components in the thus-
 10 obtained expanded graphite sheet and the results of a test for an oxidative ablation factor of the sheet are shown in Table 9. The values in the composition of components in the table are expressed in % by weight. The oxidative ablation factor in the expanded graphite sheet was evaluated by the
 15 same method as in the previous examples.

Table 9

	Comparative Example			
	6	7	8	9
Expanded graphite	96	92	88	84
Monobasic aluminum phosphate	4	8	12	16
Weight loss ratio	43%	39%	25%	24%

The expanded graphite sheets of Examples 1 to 28 contain phosphate and the phosphorus pentoxide formed by
 20 dehydration reaction. Therefore it is clear that the sheets

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exhibit a synergistic effect due to the two compounds even under high temperature conditions of 700°C, and the sheets show very low values in the oxidative ablation factor (weight loss ratio) and have heat resistance. On the other hand, the expanded graphite sheets of Comparative Examples containing either phosphoric acid or phosphate in the expanded graphite display a high oxidative ablation factor (weight loss ratio). Among others, it is clear that the expanded graphite sheets containing phosphate alone (Comparative Examples 6 to 9) show significantly high oxidative ablation factor and accordingly are inferior in heat resistance.

The expanded graphite sheets of Examples 8 and 15 have properties as shown in Table 10.

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Table 10

		Unit	Ex.8	Ex.15	Known product
Thickness		mm	0.37	0.36	0.38
Measured density		g/cm ³	1.07- 1.13	1.07- 1.13	1.07- 1.13
Tensile strength		Kgf/cm ²	50.4	52.1	55.3
Com- press- ibility	70 kgf/cm ²	%	16.4	21.7	18.9
	350 kgf/cm ²		40.7	44.7	41.5
	70 kgf/cm ²		39.5	30.6	38.6
Recov- ery	350 kgf/cm ²	%	18.3	17.2	19.0
	70 kgf/cm ²				
Stress relaxation		%	1.5	1.2	0.8
Flexi- bility	Width- wise	Fre- quency	10	12	13
	Length- wise		20	23	23
Electrical resistance (plane- wise)		$\mu\Omega$ cm	870	810	850
Oxidative ablation (700°C/3 hr)		%	5	5	98

It is evident from Table 10 that the expanded graphite sheets of Examples 8 and 15 which show a very low oxidative ablation factor and heat resistance have inherent properties of expanded graphite sheets without any degradation, and are comparable in properties with known expanded graphite sheets. The known product shown in Table 10 is a commercially available product manufactured by Toyo Tanso Co., Ltd., trade name "Model No. PF-38D". The

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flexibility in Table 10 was evaluated by a tester shown in Fig.2. A sample with a breadth of 10 mm and a length of 100 mm (expanded graphite sheet) was alternately bent at an angle of 90 degrees. The flexibility was evaluated in terms of bending frequency as counted until the sample became broken. In Fig.2, the sample is designated 1, a 50 g weight is indicated at 2 and the bending range is designated 3.

As apparent from the Examples, the expanded graphite sheets of the invention, due to specified amounts of phosphorus pentoxide and phosphate in the sheet, show heat resistance and a markedly low oxidative ablation factor even under high temperature conditions of 700°C or higher, and possess inherent properties of expanded graphite sheets without any degradation which are comparable in properties with conventional expanded graphite sheets.

Industrial Applicability of the Invention

As stated above, the expanded graphite sheets of the invention are remarkable in heat resistance and resistance to oxidative ablation and can be effectively used as gaskets, sealings, heat-insulating materials, cushion materials, etc.

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CLAIMS:

1. A heat-resistant, expanded graphite sheet containing phosphorus pentoxide and phosphate.

2. The heat-resistant expanded graphite sheet
5 according to claim 1, wherein the content of phosphorus pentoxide is 0.05 to 5.0% by weight and the content of phosphate is 1 to 16% by weight.

3. The heat-resistant, expanded graphite sheet according to claim 1 or 2, wherein the phosphate is
10 selected from monobasic lithium phosphate, dibasic lithium phosphate, monobasic calcium phosphate, dibasic calcium phosphate, monobasic aluminum phosphate and dibasic aluminum phosphate.

4. The heat-resistant, expanded graphite sheet
15 according to any one of claims 1 to 3, wherein the sheet is less than 10% in the oxidative ablation factor on exposure to the air at a temperature of 700°C for 3 hours.

5. A method for producing a heat-resistant, expanded graphite sheet, the method comprising adding phosphate to
20 an acid-treated graphite material treated with a strong acid and phosphoric acid.

6. A method for producing a heat-resistant, expanded graphite sheet, the method comprising adding phosphoric acid and phosphate to an acid-treated graphite material
25 treated with a strong acid.

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7. The method according to claim 5 or 6, wherein the phosphoric acid is selected from orthophosphoric acid, metaphosphoric acid, polyphosphoric acid and polymetaphosphoric acid.

5 8. The method according to any of claims 5 to 7, wherein the phosphate is selected from monobasic lithium phosphate, dibasic lithium phosphate, monobasic calcium phosphate, dibasic calcium phosphate, monobasic aluminum phosphate and dibasic aluminum phosphate.

10 9. A heat-resistant, expanded graphite sheet prepared by the method for producing a heat-resistant, expanded graphite sheet according to any one of claims 5 to 8, wherein the sheet contains 0.05 to 5.0% by weight of phosphorus pentoxide, and 1 to 16% by weight of phosphate.

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Abstract of Disclosure

An object of this invention is to provide an expanded graphite sheet which shows a low oxidative ablation factor in the air even when exposed to the air
5 under high temperature conditions of 700°C or higher for a long time and which is excellent in heat resistance and satisfactory in other properties required by this kind of expanded graphite sheet. The object of the invention can be achieved due to the presence of phosphorus pentoxide and
10 phosphate in the sheet.

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Fig1

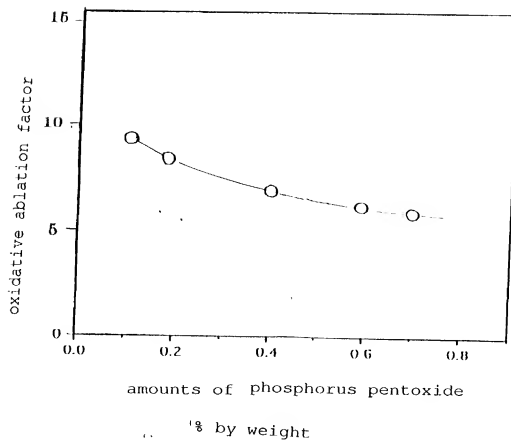
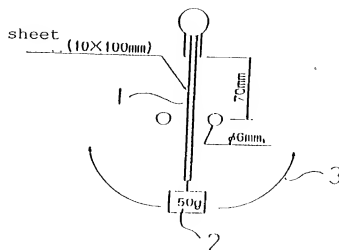


Fig 2



Docket No. 107312-00001

ARENT FOX KINTNER PLOTKIN & KAHN, PLLC

Declaration For U.S. Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

(Insert Title) HEAT-RESISTANT EXPANDED GRAPHITE SHEET AND METHOD FOR PRODUCTION OF THE SAME

the specification of which is attached hereto unless the following box is checked:

☒ was filed on July 13, 2000 As PCT International Application
 Number PCT/JP00/04717 and was amended on _____
 and/or was filed on _____ As U.S. Patent Application
 Number _____ and was amended on _____

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate or PCT International Application having a filing date before that of the application(s) for which priority is claimed:

(List prior foreign applications)	200493-1999 (Number)	Japan (Country)	14 July 1999 (Day/Month/Year Filed)	Priority Claimed <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
	(Number)	(Country)	(Day/Month/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No
	(Number)	(Country)	(Day/Month/Year Filed)	<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

☐ See attached list for additional prior foreign or provisional applications.

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) or §365(c) of any PCT International application(s) designating the United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior application(s) (U.S. or PCT) in the manner provided by the first paragraph of 35, U.S.C. §112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(List prior U.S. Applications or PCT International applications designating the U.S.)	(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
	(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

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The undersigned hereby authorizes the U.S. attorneys named herein to accept and follow instructions from the undersigned's assignee, if any, and/or, if the undersigned is not a resident of the United States, the undersigned's domestic attorney, patent attorney or patent agent, as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and the undersigned. In the event of a change in the person(s) from whom instructions may be taken, the U.S. attorneys named herein will be so-notified by the undersigned.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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